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Magnetron sputtering growth of $InAs_{0.3}Sb_{0.7}$ films on (1 0 0) GaAs substrates: Strong effect of growth conditions on film structure

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Abstract

The growth of highly lattice-mismatched $InAs_{0.3}Sb_{0.7}$ films on (1 0 0) GaAs substrates by magnetron sputtering has been investigated and even epitaxial $InAs_{0.3}Sb_{0.7}$ films have been successfully obtained. A strong effect of the growth conditions on the film structure was observed, revealing that there was a growth mechanism transition from three-dimensional nucleation growth to epitaxial layer-by-layer growth mode when increasing the substrate temperature. A qualitative explanation for that transition was proposed and the critical conditions for the epitaxial layer-by-layer growth mode were also discussed.

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1. Introduction

Recently, the $InAs_xSb_{1-x}$ alloy system has attracted considerable interest due to its potential applications in infrared sources and detectors, especially for the long-wavelength ($\lambda > 8\,\mu m$) spectral region. At present, $Hg_{1-x}Cd_xTe$ is the dominant material system for long-wavelength infrared applications. However, it suffers from instability and nonuniformity over a large area due to the weakness of mercury bonding in the compound [1] and high mercury vapor pressure during material growth [2], respectively. With satisfying material properties and highly advanced III–V semiconductor processing

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technologies, $InAs_xSb_{1-x}$ could be a promising alternative to $Hg_{1-x}Cd_xTe$. With its composition in mid-range ($0.2<x<0.7$), $InAs_xSb_{1-x}$ can exhibit large positive optical bowing due to ordering in the alloy [3–6]. A cut-off wavelength up to 14 μm at room temperature has been reported for p-type $InAs_{0.23}Sb_{0.77}$ grown on GaAs substrates by low-pressure metalorganic chemical vapor deposition (LP-MOCVD) [2]. GaAs is an excellent substrate for its high quality and low cost; moreover, it helps to integrate detection and signal processing circuits and reduce parasitic capacitances.

For the large lattice mismatch between $InAs_xSb_{1-x}$ and GaAs ($7.2\%<\Delta a/a<14.6\%$) and the difficult incorporation of As into InSb due to the miscibility gap in the phase diagram [7,8], it is hard to obtain mid-range $InAs_xSb_{1-x}$ films of high material quality grown on GaAs substrates. So far, epitaxial films of mid-range $InAs_xSb_{1-x}$ have been successfully grown on GaAs substrates by molecular beam epitaxy (MBE) [8–11] and MOCVD [2,12,13]. However, hitherto no report in the literature about the growth of $InAs_xSb_{1-x}$ films on GaAs substrates by magnetron sputtering has been found. Comparing with MBE and MOCVD, magnetron sputtering is more economical and convenient: the equipments of MBE and MOCVD are very expensive and their maintenances are complicated, and the growth costs of MBE and MOCVD are quite high; moreover, source materials of MOCVD, i.e. metalorganic gases, are all extremely toxic. Furthermore, intentional doping to $InAs_xSb_{1-x}$ films for magnetron sputtering could be easily realized in two ways: (i) directly add some corresponding impurities (i.e. Te or Se for n-type and Cd or Zn for p-type) to the $InAs_xSb_{1-x}$ target; (ii) add one target of corresponding impurities co-sputtering with the $InAs_xSb_{1-x}$ target. In this letter, magnetron sputtering growth of $InAs_{0.3}Sb_{0.7}$ films on (1 0 0) GaAs substrates was investigated and even epitaxial $InAs_{0.3}Sb_{0.7}$ films were successfully procured.

2. Experimental procedure

Samples were prepared in a radio frequency (RF) magnetron sputtering system with a base pressure of 3×10^{-5} Pa. An 8.5-cm-diameter $InAs_{0.3}Sb_{0.7}$ (99.9999% pure) disk was used as target. The substrates were $20\times20\times0.5\,mm^3$ well-polished, semi-insulating (1 0 0) GaAs wafers, which were rinsed successively with tetrachloromethane, acetone, ethanol and de-ionized water in ultrasonic baths, and then etched in a solution of H_2SO_4:H_2O_2:H_2O = 5:1:1 (volume ratio) before being put into the sample introduction chamber. Prior to deposition, the substrate mounted in the growth chamber was heated to 600 °C for 10 min and then the target was sputter etched for 10 min while the substrate was shielded. After the preprocessing of substrates and the target, sputtering growth began and lasted for 3–6 h under certain conditions.

In general, growth conditions have determinative influences on material properties by regulating growth rate and temperature, of which substrate temperature and RF power are the most important parameters in magnetron sputtering. Hence, to gain an insight into these influences, the two parameters were altered and the others kept constant when growing different samples. Substrate temperatures (T_s) of 150–500 °C and RF powers (P_{RF}) of 30–100 W were applied for different samples. The sputtering gas was 99.999% pure argon with a pressure of 0.13 Pa, and the distance between the target and substrate was fixed at 4 cm.

The morphologies of the grown films were characterized by scanning electron microscope (SEM), and energy dispersive X-ray analysis (EDAX) of SEM was used for compositional analysis of the films. The structure of the films was characterized by X-ray diffraction (XRD). An X'Pert Pro MPD diffractometer was used for conventional $\omega-2\theta$ scanning. Since the diffractometer is equipped with an X'CELERATOR detector array, it is rather sensitive to weak reflections from samples. The material quality of the grown epitaxial films was elementarily examined by Hall measurement at room temperature and a Philips X'Pert high-resolution X-ray diffractometer with a resolution up to 0.0001°, which was used for measuring the rocking curves.

3. Results and discussion

The surfaces of all the $InAs_xSb_{1-x}$ films look mirror shiny to the naked eye, and are also very smooth by SEM. Fig. 1 shows the cross-section SEM image of sample A grown at $T_s = 350\,^\circ C$ and $P_{RF} = 30\,W$, in which a trim layer with a sharp interface lying on the substrate can be observed. Since it is a typical cross-section image of all grown films, the surface flatness and thickness uniformity of the films are excellent. The growth rates were obtained based on the growth time and thicknesses measured from the SEM images, and the corresponding results are shown in Table 1. It can be found out that the growth rates are controlled primarily by the applied RF powers, demonstrating that the growth process is mass-controlling. As it is well known that generally the composition of the film grown by magnetron sputtering using one target will be consistent with that of the target, the results of EDAX quantitative calculation, which are also shown in Table 1, follow this rule. The atomic percent of the constituent elements in the films are all in the vicinity of that in the target at an error level of $\pm$2at.%, which is acceptable for EDAX. Therefore, it is reasonable to draw a conclusion that the growth conditions have little influence on the composition of the films, since it is determined by the composition of the target.

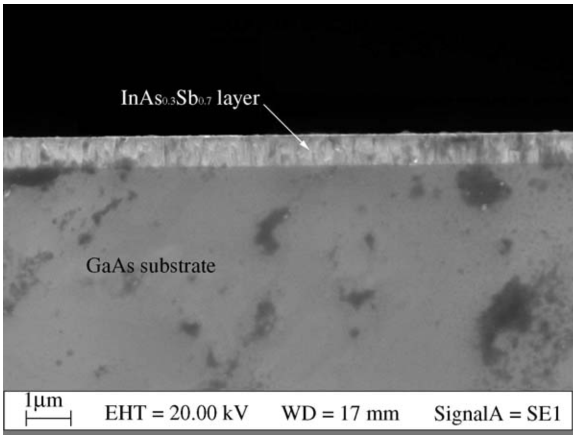

Fig. 1. Cross-section SEM image of sample A grown at $T_s = 350\,^\circ C$ and $P_{RF} = 30\,W$; it is a typical cross-section image of all the grown films.

Fig. 2 shows a series of XRD patterns of samples grown under different conditions. All the reflections in these patterns are from a single phase $InAs_xSb_{1-x}$, and its composition x equals approximately 0.3 according to Vegard's law. It keeps remarkable consistence with the result of the aforementioned EDAX analysis, indicating that $InAs_{0.3}Sb_{0.7}$ films have been successfully grown on GaAs substrates by magnetron sputtering. Nevertheless, from those patterns diverse film structures can be seen as of different growth conditions. It was found experimentally that substrate temperature had a predominant influence on film structure. The four patterns, Fig. 2 (a)–(d), illustrate a transition process of the film structure with the

Table 1
EDAX results and corresponding growth rates and conditions of the grown films

Sample	Substrate temperature T_s (°C)	RF power P_{RF} (W)	Growth rate r_g (μm/h)	EDAX results		
				In at.%	As at.%	Sb at.%
A	350	30	0.25	52	14	34
B	400	30	0.25	51	13	36
C	300	50	0.39	49	17	34
D	400	50	0.40	48	16	36
E	450	60	0.50	49	14	37
F	500	60	0.48	52	14	34
G	420	100	0.93	51	16	33
H	500	100	0.91	—	—	—

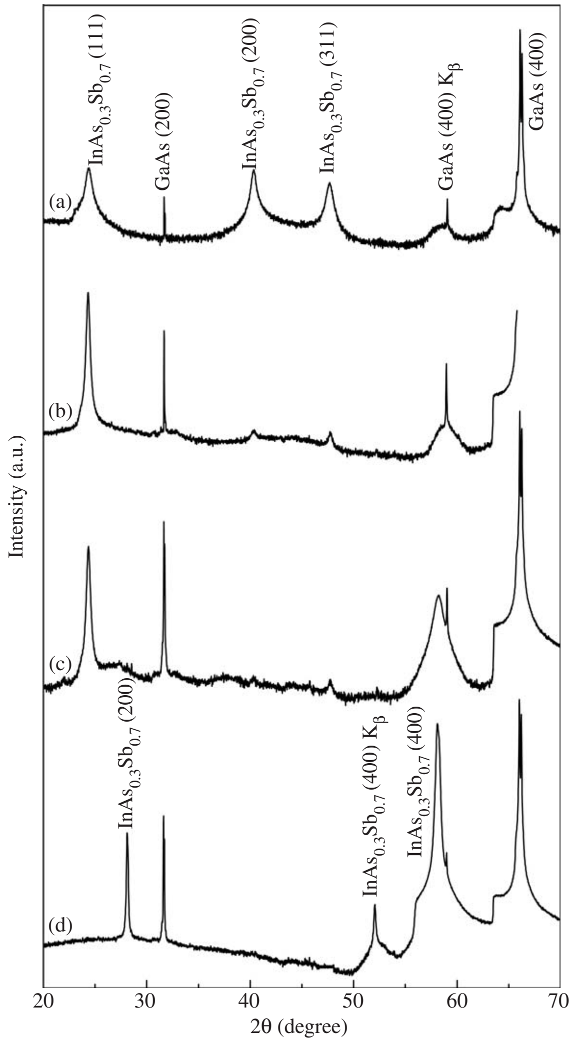

Fig. 2. XRD patterns of samples grown at (a) $T_s = 150\,°C$, $P_{RF} = 50\,W$; (b) $T_s = 250\,°C$, $P_{RF} = 50\,W$; (c) $T_s = 300\,°C$, $P_{RF} = 50\,W$ (sample C); (d) $T_s = 400\,°C$, $P_{RF} = 50\,W$ (sample D).

substrate temperature: as the substrate temperature increased, at first the film was polycrystalline with random orientation (Fig. 2(a)), and then turned to highly (1 1 1)-preferred orientation (Fig. 2(b)); after this the epitaxial (1 0 0) orientation grew stronger (Fig. 2(c)) until it finally became entirely epitaxial (Fig. 2(d)). This process may suggest a transition of growth mechanism from three-dimensional (3D) nucleation growth to epitaxial layer-by-layer growth mode: when the substrate temperature was low, such as 150 °C, the growth mechanism was 3D nucleation growth, namely, sputtered atoms from the target firstly formed islands of $InAs_{0.3}Sb_{0.7}$ with random orientations on the substrate, and only those islands larger than a critical size could grow, eventually forming an $InAs_{0.3}Sb_{0.7}$ film; however, when the substrate temperature was high enough, such as 400 °C, the sputtered atoms would directly form $InAs_{0.3}Sb_{0.7}$ film along the lattice of the substrate, i.e. the growth mechanism became an epitaxial layer-by-layer growth mode.

Fig. 3 shows a figurative sketch map resembling the forming process of $InAs_{0.3}Sb_{0.7}$ films: state 1 corresponds to polycrystalline film with random orientation, which is easy to come into being but has high free energy; state 2 corresponds to polycrystalline film with (1 1 1)-preferred orientation, which has lower free energy than state 1 because the (1 1 1) plane has the smallest surface energy, but a barrier energy E_1 needs surmounting to be there; state 3, corresponding to epitaxial film, has the lowest free energy since interface energy is dramatically reduced, but a barrier energy E_2 higher than E_1 blocks its formation. As we know, the higher the substrate temperature, the more the thermal activation energy (E_T) sputtered atoms absorbed on a substrate surface have, and all systems have the tendency to be in a state with the lowest free energy. Therefore, when substrate temperature is low, the atoms do not have enough energy ($E_T < E_1$) to overcome the barriers; then

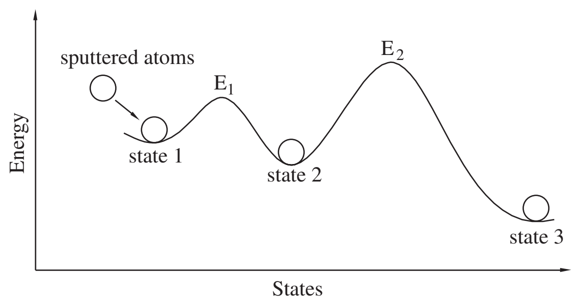

Fig. 3. Figurative sketch map resembling the forming process of an $InAs_{0.3}Sb_{0.7}$ film. State 1: polycrystalline film with random orientation; state 2: polycrystalline film with (1 1 1)-preferred orientation; state 3: epitaxial film.

the system is confined to state 1, which is easiest to get from the initial state of the system. However, with substrate temperature increasing, the atoms will get enough energy to overcome some barrier (E_1 or E_2); thereupon, the system can reach the corresponding state. Thus, the transition process mentioned above could get a qualitative explanation. It should be noted that the free energies of the states are based on thermodynamics, but the barrier energies E_1 and E_2 are based on kinetics. Actually, E_1 and E_2 refer to the activation energies of the (1 1 1)-preferred orientation nucleation growth process and the epitaxial layer-by-layer growth process, respectively. That is to say, E_1 and E_2 consist of the driving forces of all the physical processes involved in the corresponding growth process, such as nucleation, escaping from metastable states and diffusion to the right positions.

Of course, the epitaxial layer-by-layer growth mode is preferred rather than the 3D nucleation growth; hence, the conditions of the epitaxial layer-by-layer growth mode are what we care most. According to the experimental results, two points are crucial for the epitaxial layer-by-layer growth mode. First, the substrate temperature must be higher than a threshold value to furnish the sputtered atoms with enough energy to overcome the barrier energy E_2. We have grown $InAs_{0.3}Sb_{0.7}$ film on Si substrate in the same conditions with sample D, and its XRD pattern is shown in Fig. 4, indicating that the film is still polycrystalline with (1 1 1)-preferred orientation. It illustrates that E_2 correlates with the interfacial energy between $InAs_{0.3}Sb_{0.7}$ film and substrate, and obviously E_2 of Si substrate is larger than that of GaAs substrate. Second, the growth rate must be lower than a threshold value, or other orientations will break into the epitaxial layer-by-layer growth. Fig. 5 shows the XRD pattern of sample G grown at 420 °C with a growth rate of 0.93 μm/h, in which, besides the (4 0 0) and (2 0 0) reflections, the (1 1 1) reflection of $InAs_{0.3}Sb_{0.7}$ also appeared. It illustrates that although at 420 °C the atoms absorbed on substrate surface have enough energy to surmount the barrier E_2, the growth rate of 0.93 μm/h is too high for the epitaxial layer-by-layer growth process at that temperature. Nevertheless, the threshold value of growth rate can be enhanced by increasing substrate temperature, which is based on the experimental fact that although sample H was grown at the same growth rate with sample G, but at a higher substrate temperature of 500 °C, the (1 1 1) reflection of $InAs_{0.3}Sb_{0.7}$ was extinct from its XRD pattern. It can be inferred that the threshold value of growth rate lies on the diffusion speed of the atoms absorbed on the substrate surface. Note that by MBE [8,10] or MOCVD [2,12] epitaxial layer-by-layer growth of $InAs_xSb_{1-x}$ films on GaAs substrates with a growth rate of about 1 μm/h

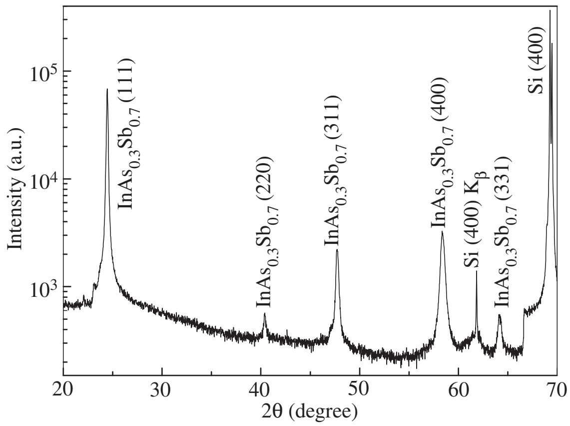

Fig. 4. XRD patterns of the sample grown on (1 0 0) Si substrate at $T_s = 400\,°C$ and $P_{RF} = 50\,W$.

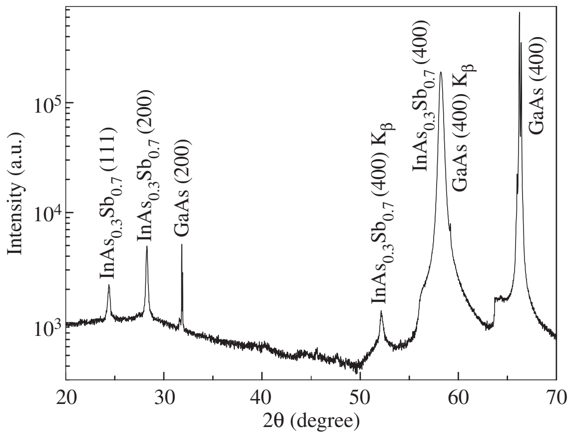

Fig. 5. XRD patterns of sample G grown at $T_s = 420\,°C$ and $P_{RF} = 100\,W$.

can be achieved at the substrate temperature range of 400–480 °C, and one could see some differences in growth mechanism between magnetron sputtering and MBE or MOCVD.

Fig. 6 shows the rocking curves (RC) from $InAs_{0.3}Sb_{0.7}$ (4 0 0) reflection of samples D and F, and Table 2 shows the corresponding full-widths at half-maximum (FWHM) and results of the Hall measurement. The data in Table 2 show that sample F exhibits better quality than sample D, suggesting that growth conditions still have a pronounced influence on material quality even though the epitaxial conditions are already met. The Hall mobilities of the samples are all relatively low compared with those grown by MBE [8,10] and MOCVD [12]. Considering the high carrier concentrations ($>10^{18}\,cm^{-3}$) in the samples, it should be mainly attributed to the impurities unintentionally but heavily doped to the $InAs_{0.3}Sb_{0.7}$ films. The impurities may be introduced from the $InAs_{0.3}Sb_{0.7}$ target, magnetron sputtering system and sputtering gas. Because of the purity of the $InAs_{0.3}Sb_{0.7}$ target was high up to 6N, the impurities may mainly come from the magnetron sputtering system or be brought into the system by the sputtering gas. In this regard, magnetron sputtering manifested a drawback in comparison with MBE and MOCVD, namely, magnetron sputtering systems cannot provide an ultra-clean growth environment like MBE and MOCVD systems do. Hence, reducing the unintentionally doped impurities and optimizing the growth conditions are two ways by which the quality of the grown films may be improved. Detailed investigation on the properties of $InAs_xSb_{1-x}$ films grown on GaAs substrates by magnetron sputtering awaits more efforts.

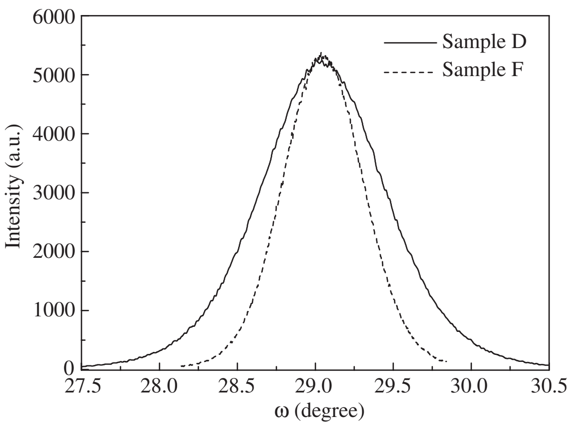

Fig. 6. Rocking curves of samples D and F: solid line for sample D anddashed line for sample F. For comparison, they were processed to the same maximum height.

Table 2
FWHM of RC and results of Hall measurement at room temperature of samples D and F

Sample	FWHM of RC (deg)	Hall mobility ($cm^2/V\,s$)	Carrier concentration (n type) ($\times 10^{18}\,cm^{-3}$)
D	0.91	924	6.53
F	0.63	1773	4.45

4. Conclusion

In conclusion, highly lattice-mismatched $InAs_{0.3}Sb_{0.7}$ films have been successfully grown on (1 0 0) GaAs substrates by magnetron sputtering. Experimental results revealed that the growth process was mass-controlling and there was a growth mechanism transition from 3D nucleation growth to epitaxial layer-by-layer growth mode when increasing the substrate temperature. For the epitaxial layer-by-layer growth mode, two critical conditions should be met, including that the substrate temperature must be higher than a threshold value and the growth rate must be lower than one. The material quality of the grown epitaxial films may be improved by reducing the unintentionally doped impurities and optimizing the growth conditions.

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